

# Few-body reference data for multicomponent formalisms: Light nuclei molecules

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We present full quantum statistical energetics of some electron-light nuclei systems. This is accomplished with the path integral Monte Carlo method. The effects on energetics arising from the change in the nuclear mass are studied. The obtained results may serve as reference data for the multicomponent density functional theory calculations of light nuclei system. In addition, the results reported here will enable better fitting of today's electron-nuclear energy functionals, for which the description of light nuclei is most challenging, in particular.

Density functional theory (DFT) is among the most successful approaches to calculate the electronic structure of atoms, molecules and solids. A similar approach, however, including more degrees of freedom was introduced in 2001 by Kreibich and Gross [1], and is called as multicomponent density-functional theory (MCDFT). In contrast to original form of the DFT, MCDFT enables the complete quantum treatment of many particle systems consisting of electrons and nuclei. As is well known, the original form of DFT incorporates the Born–Oppenheimer approximation for the nuclei [2, 3].

With the MCDFT approach it is possible to extend the success of DFT into an entirely new field of applications, such as first-principles calculation of electron-phonon coupling in solids [4, 5], polaronic motion [6] and positron scattering and annihilation [7–9]. That is, with MCDFT physical phenomena that depend on a strong coupling between electronic and nuclear motion can be evaluated from first principles.

The original DFT is also known for its need of good functional forms, especially for the exchange and correlation functional. One of the most widely employed functional is the so-called local density approximation (LDA), which uses the Monte Carlo data of the free electron gas [10] as a basic input. Proper functional forms are also needed in the MCDFT scheme, for the electron-nuclear energy functional [11, 12], in particular. For the present, the absence of good multicomponent reference data is slowing down the development of new functional forms for the MCDFT. The main difficulties are encountered in the description of light nuclei.

In this brief report, we will provide few-body reference data for light nuclei systems, which can be used in the development of better MCDFT functionals and improving the present fits. This is accomplished with full quantum statistical simulations using path integral Monte Carlo (PIMC) approach [13]. The nuclear mass is given values ranging from that of a positron to that of a proton described by the following processes:  $x^+e_2^-$ ,  $x_2^+e^-$ ,  $x_2^+e_2^-$  and  $x^+p^+e_2^-$ , where  $x^+$  goes from positron ( $e^+$ ) to proton ( $p^+$ ). A more detailed description of our approach is given in Ref. [14].

According to the Feynman formulation of the quantum

statistical mechanics [15] the partition function for interacting distinguishable particles is given by the trace of the density matrix:

$$Z = \text{Tr } \hat{\rho}(\beta) = \int dR_0 dR_1 \dots dR_{M-1} \prod_{i=0}^{M-1} e^{-S(R_i, R_{i+1}; \tau)},$$

where  $\hat{\rho}(\beta) = e^{-\beta \hat{H}}$ ,  $S$  is the action,  $\beta = 1/k_B T$ ,  $\tau = \beta/M$ ,  $R_M = R_0$  and  $M$  is called the Trotter number. In this paper, we use the pair approximation in the action [13, 16] for the Coulomb interaction of charges. Sampling in the configuration space is carried out using the Metropolis procedure [17] with multilevel bisection moves [18]. The total energy is calculated using the virial estimator [19].

In the following we use atomic units, where the lengths, energies and masses are given in units of the Bohr radius ( $a_0$ ), hartree ( $E_h$ ) and free electron mass ( $m_e$ ), respectively. The statistical standard error of the mean (SEM) with 2SEM limits is used as an error estimate for the observables.

In our model, all the particles are described as "boltzmannons", i.e. they obey the Boltzmann statistics. For the present study the particles involved can be treated accurately as distinguishable particles. This is possible by assigning spin-up to one electron and spin-down to the other one, and applying the same for the positive particles. This is accurate enough, as long as the thermal energy is well below that of the lowest electronic triplet excitation,  $\Delta E_{st}$ . For the systems in consideration  $\Delta E_{st} > 0.18 E_h$ , the smallest being that of the  $\text{Ps}_2$  molecule [20, 21]. For more details on our model, see Ref. [14].

In the simulations we use  $m_e = 1 = m_{e^+}$  as the mass of the electrons and the positron, and for the protons we use  $m_p = 1836.1527 m_e$ . The simulations are carried out at 300 K temperature, and for the Trotter number we have chosen  $M = 8192$ . This leads to "time-step"  $\tau = \beta/M \approx 0.1285 E_h^{-1}$ , which ensures good enough accuracy in the case of light nuclei — the error is of order  $\mathcal{O}(\tau^3)$ . The simulations apply the minimum image convention and a cubic simulation cell,  $V = (300 a_0)^3$ .

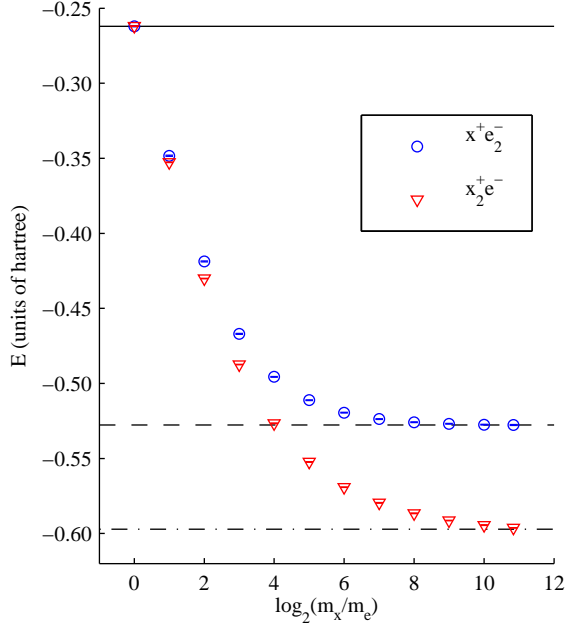


Figure 1: Total energy as a function of mass of the nuclei, i.e. positive particles. Blue circles show the energy for  $x^+e_2^-$ , and red down-triangles that for  $x_2^+e^-$ , where  $x^+$  goes from  $e^+$  to  $p^+$ . The reference energies are given as solid line, dashed line and dash-dotted line corresponding to  $\text{Ps}^-$  (as well as  $\text{Ps}_2^+$ ),  $\text{H}^-$  and  $\text{H}_2^+$ , respectively.

In Figs. 1 and 2 we show the total energy as a function of mass of the nuclei, i.e. the positive particles: On the left  $x^+$  is equal to a positron, on the right  $x^+$  corresponds to a proton, and in the middle region we assign ten different masses for the  $x^+$  particle.

The total energies are also given in Table I. The time-step error affects mainly the fourth decimal in the total energies, which can be validated by comparing the end-point values in Table I to high-accuracy zero Kelvin results. The comparison shows that the difference between high accuracy results and our PIMC values is less than  $0.00094E_h^{-1}$ , which also confirms that the order of the time-step error is  $\mathcal{O}(\tau^3)$ . Since the fourth decimal is also uncertain due to statistical error estimate, the present time-step error is considered acceptable. All energies given in Table I are from separate long enough simulations. Due to the finite temperature present in our simulations there is a small possibility for these molecules to dissociate even at the temperature of 300 K, however, none of our simulations experienced dissociation.

The main difficulties in the MCDFT are related to the description of light nuclei. Protons in small systems are already treated reasonably. However, there definitely is room for improvement in that case, and especially in case of positronic systems. The data presented in Table I will serve as a good reference data in the development and fitting of electron-nuclear energy functionals. It enables

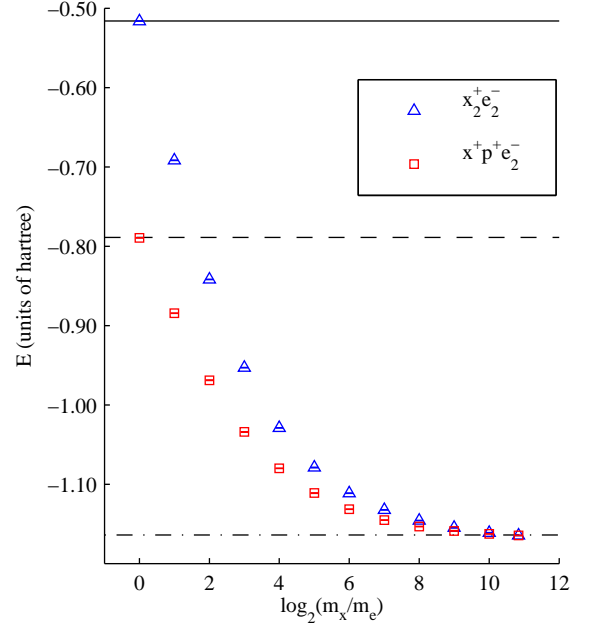


Figure 2: Total energy as a function of mass of the nuclei, i.e. positive particles. Blue up-triangles show the energy for  $x_2^+e_2^-$ , and red squares that for  $x^+p^+e_2^-$ , where  $x^+$  goes from  $e^+$  to  $p^+$ . The reference energies are given as solid line, dashed line and dash-dotted line corresponding to  $\text{Ps}_2$ ,  $\text{PsH}$  and  $\text{H}_2$ , respectively.

one to gradually go towards proper description of the lightest and most difficult "nucleus", i.e. the positron.

It should be pointed out, that proper density dependent reference data will be essential for the success of MCDFT. Obtaining such results is computationally demanding, however, the authors of this paper are already

Table I: Total energies at different nuclear masses, see also Figs. 1 and 2. Energies are given in units of hartree with 2SEM error estimates. Reading from up to down the  $x^+$  in the table goes from positron to proton — the mass of the particle increases.

$\log_2(m_x/m_e)$	$x^+e_2^-$	$x_2^+e^-$	$x_2^+e_2^-$	$x^+p^+e_2^-$
0.0000	-0.2620(4)	-0.2620(1)	-0.5163(2)	-0.7895(3)
1.0000	-0.3483(3)	-0.3526(1)	-0.6918(2)	-0.8845(3)
2.0000	-0.4187(3)	-0.4301(2)	-0.8418(3)	-0.9690(4)
3.0000	-0.4670(2)	-0.4874(2)	-0.9531(3)	-1.0341(3)
4.0000	-0.4956(2)	-0.5266(2)	-1.0291(3)	-1.0800(3)
5.0000	-0.5111(2)	-0.5523(2)	-1.0790(3)	-1.1112(3)
6.0000	-0.5195(2)	-0.5692(2)	-1.1114(3)	-1.1315(3)
7.0000	-0.5237(2)	-0.5796(2)	-1.1323(3)	-1.1451(3)
8.0000	-0.5258(2)	-0.5866(2)	-1.1458(3)	-1.1533(3)
9.0000	-0.5269(2)	-0.5913(2)	-1.1549(3)	-1.1588(3)
10.0000	-0.5275(2)	-0.5944(2)	-1.1612(3)	-1.1627(3)
10.8425	-0.5277(3)	-0.5962(2)	-1.1646(3)	-1.1647(3)

working on it. For now, the results of this paper give useful complementary information on the energetics of small light nuclei systems, which can be used in the finding better fits for the functionals.

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